PHASE DISTRIBUTION OF PCDD/Fs AND co-PCBs DURING PVC COMBUSTION AT VARIOUS TEMPERATURES

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Introduction

During the combustion of Polyvinyl chloride (PVC), various chlorinated pollutants such as polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurnas (PCDD/Fs) and Polychlorinated biphenyls (PCBs) are formed that are carcinogenic pollutants for the environment[1]. Over several years, many studies have been conducted in the laboratory or the pilot scale to investigate the combustion behavior and the associated hazardous emission from PVC[2,3]. In addition, many investigators have studied an extraction and clean-up method of PCDD/Fs and PCBs[4].

However, the phase distribution of PCDD/Fs and co-PCBs at various temperatures has been studied not much. Information about the phase distribution of PCDD/Fs and co-PCBs is useful to set up a sampling apparatus or design a treatment utility. In this study, the phase distribution and isomer patterns of PCDD/Fs and co-PCBs was compared at various temperatures during PVC combustion using laboratory scale incinerator.

Method and Materials

Combustion Apparatus

PVC (as powder) applied was free of additives and purchased from Aldrich. Combustion apparatus, which was batch type one-stage equipment, consisted of a vertical electric muffle furnace fitted with a quartz tube, 40 mm I.D and 500 mm height (Figure 1). For simplicity of sample insertion and induction of turbulence, combustion apparatus was utilized downstream vertical type. A high-purified air (>99.999%) was applied at the flow rate of 2 L/min. Experimental temperature of the furnace was adjusted at 300, 600 and 900 , respectively. Upon reaching the temperature of furnace each condition, a platinum sample vessel containing 0.5 g of PVC was inserted from the top and positioned in the middle of furnace. Thermal decomposition of PVC occurred by 3 min after insertion and flue gas was passed through sampling device. The efficient and pertinent sampling device was evaluated as described by Kim[5]. The sampling device used consist of silica glass microfibre filter followed by XAD- resin, backup solvent (Toluene 50ml). Each part was pretreated and analyzed for PCDD/Fs and co-PCBs, respectively. The concentrations of oxygen, carbon monoxide and nitrogen oxides were measured continuously.

Clean-up & Analysis

After cooling the furnace to room temperature, glass fiber filter, XAD- adsorbent and residues in the vessel were soxhlet extracted with toluene for 24 hours, respectively. Sample extraction and clean-up were carried out in accordance with Korean Standard Method of Air Pollution. The extracts and washes were replaced by 100 ml n-hexane prior to sulfuric acid treatment. Co-PCBs and PCDD/Fs ^{13}C-Labelled compounds were added to each sample. And then the sample was first treated with concentrated H_2SO_4 and purified by multi-layered silica gel and alumina column. The fraction containing PCDD/Fs was concentrated under a gentle stream of nitrogen. The fraction including PCBs was conducted in the same way with PCDD/Fs. The analysis for PCDD/Fs and PCBs was performed on selected ion monitoring (SIM) mode with a JEOL JMS-700 high resolution mass spectrometer connected with high resolution gas chromatograph (Hewlett-Packard 6890 GC).

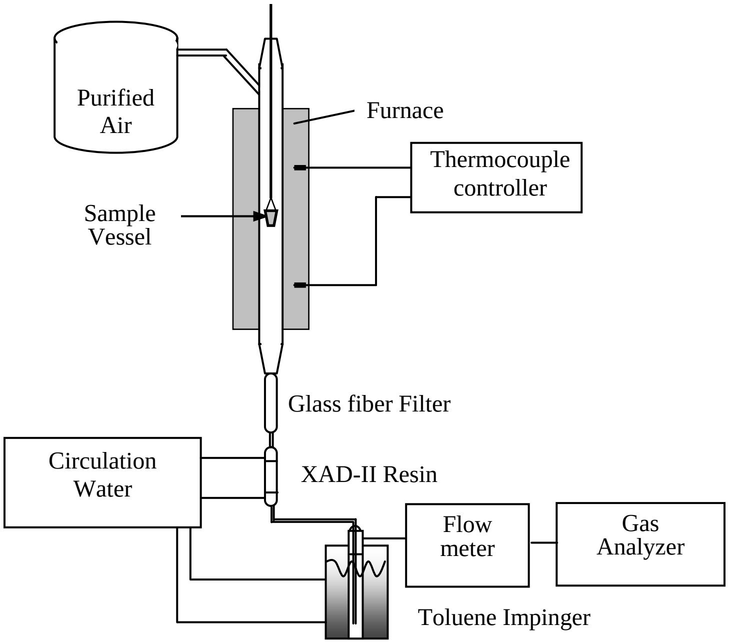

Figure 1. Experimental apparatus for PVC combustion

Results and Discussion

The distribution of gas and solid phase for each component was summarized in Table 1. Solid phase compounds were analyzed in the silica glass microfibre filter, while gas phase compounds passed through the filter and were entrapped in the XAD- resin and toluene. Carbonaceous residues remaining in the sample vessel were obtained at the temperature of 300 . In this residue, very low PCDD/Fs and PCBs were found. Most of PCDD/Fs were found in the solid phase at the temperature of 300 and 600 . At the temperature of 900 , the concentration of PCDD/Fs in the gas phase was predominant. PCBs had similar distributions with PCDD/Fs. However, at 900 , the gas phase PCBs was little higher than gas phase PCDD/Fs. The characteristics of phase distribution of PCDD/Fs and PCBs showed much different tendency at various combustion temperatures.

Total amount of PCDD/Fs and PCBs at the temperature of 600 , especially PCDFs, was very high to identify their isomer compositions. It is too low to form chlorinated pollutants at the temperature of 300 . The decomposition of PCDD/Fs and PCBs was arisen above the temperature of 900 . The ratio of PCDFs to PCDDs was increased according to combustion temperature. The total amount of PCDD/Fs emitted at 300 and 600 was greater than that of PCBs, however, the reverse tendency was showed at the temperature of 900 .

Table 1 The distribution of PCDD/Fs and PCBs at various temperatures

	300				600			900		
	XAD	Filter	Residue	Total	XAD	Filter	Total	XAD	Filter	Total
PCDDs [ng/g]	0.03 (0.5%)	5.81 (99.2%)	0.02 (0.3%)	5.86	0.10 (0.6%)	17.33 (99.4%)	17.44	0.02 (60.0%)	0.01 (40.0%)	0.03
PCDFs [ng/g]	0.03 (0.8%)	3.06 (99.2%)	0.00 (0.0%)	3.09	13.16 (9.0%)	132.90 (91.0%)	146.1	0.53 (73.9%)	0.19 (26.1%)	0.72
PCBs [ng/g]	1.05 (32.3%)	1.90 (58.3%)	0.31 (9.4%)	3.26	20.32 (24.8%)	61.75 (75.2%)	82.07	4.79 (84.3%)	0.89 (15.7%)	5.68
PCDF/D Ratio	-	-	-	0.53	-	-	8.38	-	-	24.0

Figure 2 shows the isomer patterns and the ratio of gas and solid phase for PCDD/Fs. At the temperature of 300 and 600 , highly chlorinated PCDDs (such as OCDD) and PCDFs (such as OCDF), respectively, are dominant. More PCDFs are emitted than PCDDs at the temperature of 900 . The congener patterns of solid phase at both 300 and 600 resemble in isomer composition. There are slight differences in PCDD/Fs congener patterns of gas phase at 300 and 600 , but the concentration is too small to form any conclusions about congener profile. There are no gas phase HxCDD/Fs detected at the temperature of 300 .

The isomer patterns and ratio of gas and solid phase for PCBs was illustrated in Figure 3. Low chlorinated biphenyls are dominant at the temperature 300 and 900 , however, highly chlorinated biphenyls such as deca-CBs and nona-CBs (IUPAC congener #209 and #206, respectively) are more emitted at the temperature 600 . Like PCDD/Fs, PCBs congener profiles of solid phase at the temperature 300 and 600 are similar to each other. There are, however, significantly different from the congener patterns of gas phase at 300 and 600 . The congener profile of solid and gas phase at the temperature of 900 was very similar.

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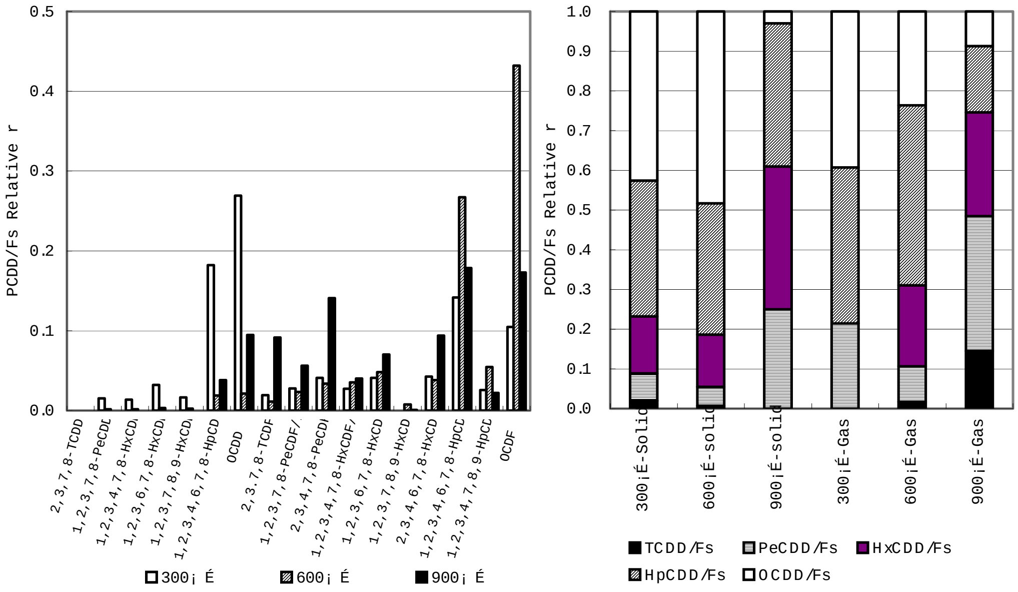
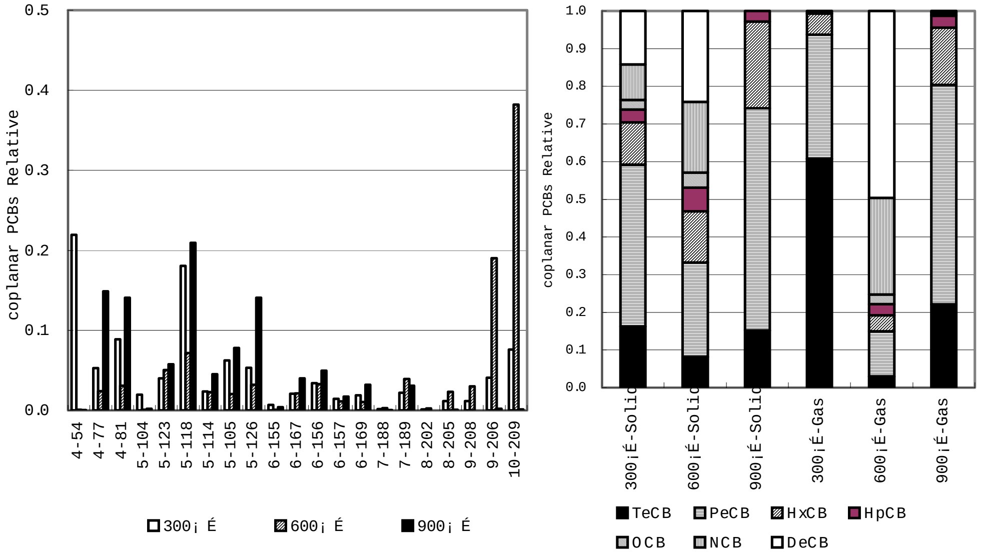


(a) Isomer pattern of PCDD/Fs (b) Ratio of PCDD/Fs

Figure 2. Isomer pattern and ratio of PCDD/Fs during PVC combustion



(a) Isomer pattern of PCBs (b) Ratio of PCBs

Figure 3. Isomer pattern and ratio of PCBs during PVC combustion